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(57) Abstract

Described is an aqueous disinfectant and hard surface cleaning composition comprising: an effective disinfecting amount of a quaternary ammonium compound; an effective amount of a spore forming microbial composition; and an effective water dispersing amount of a surfactant. The composition is used to clean a hard surface containing a diverse microbial flora. The composition cleans and disinfects by killing off undesirable microorganisms which may be causing offensive odors and leaves behind *Bacillus* spores which will then germinate and degrade any remaining ongoing residues without creating offensive odors.

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AQUEOUS DISINFECTANT AND HARD SURFACE CLEANING COMPOSITION AND METHOD OF USE

TECHNICAL FIELD

The present invention is concerned with a disinfecting and hard surface cleaning composition utilizing spore forming microbiological bacteria.

BACKGROUND OF THE INVENTION

In the general housekeeping environment in many facilities, there are numerous soiled surfaces.

In the general housekeeping environment of many facilities, there are numerous surfaces which are difficult for the custodial staff to adequately clean and maintain. The composition and/or function of these surfaces is such that they typically harbor organic soils and a diverse microbial flora that standard cleaning procedures do not effectively remove. Such surfaces include, but are not limited to, floors and walls in areas such as kitchens, restrooms, locker rooms, animal production facilities, kennels or veterinary clinics, loading docks, trash collection bins, and public transit operations.

As these surfaces accumulate soil and the natural microbial flora proliferates due to inadequate cleaning, the facility suffers two consequences. First, apparent cleanliness of the facility diminishes due to

the soil load found in these materials. Secondly, this soil load can become a major source of nuisance odors due to the biological degradation of the organics by the resident microbial population.

Current technology does not offer an effective and efficient manner with which to solve this cleaning task. The principle method of cleaning employed relies on a light to medium duty cleaner and/or cleaner/disinfectant.

These types of products are capable of removing most surface soils and in the case of a disinfectant, destroying some of the resident bacterial population. They are not, however, effective against the soils that have penetrated the surface nor does their use of fragrances to mask odor offer any residual control of these nuisances. Because of this, either effective cleaning does not take place or a multi-step process is required to be successful. The best available cleaning technology involves application of the above type product(s) to clean the surface, followed by a rinse of clear water, and the use of a biologically active product to "deep clean" the surface and control odors. Biological products based on bacteria from the genus *Bacillus* "deep clean" and control odors through the biological degradation of the organics trapped in the substrate.

The objective of this invention is to offer a single-step process by which to accomplish cleaning of these surfaces. The invention is a combination of cleaning, disinfecting, and microbiological activity in one aqueous product.

The utilization of the microbial materials is to destroy offensive odors and their source that may be present on a surface. The purpose of the antimicrobial component is to kill various types of microorganisms found on the surface which might pose health concerns or contribute to nuisance odors. The microbials remain on the surface (after

use) to continue the cleaning process through degradation of residual organics. A particularly important aspect of formulating antimicrobial products is that they remain stable for a long period of time. The microbiological materials likewise need to be stable in the presence of the other components of a cleaning composition such as the antimicrobial actives such as the quaternary ammonium compounds.

It is an object of the present invention to obtain an effective disinfectant and hard surface cleaning composition that is aqueous based.

It is an object of the present invention to obtain and utilize in combination a disinfectant, hard surface cleaning, and bacterial composition that is stable for a long period of time, but also allows the microbial material to remain active on the hard surface after the drying of the cleaning composition.

It is an object of the present invention to utilize an aqueous composition containing the genus *Bacillus* in the presence of disinfectants such as quaternary ammonium compounds.

It is an object of the present invention to perform general cleaning tasks in a more efficient manner whereby the multi-step cleaning process to clean, disinfect and control odors on hard surface substrates is decreased. The utilization of this invention will permit the saving of labor time and reduce chemical inventory.

It is an object of the present invention to utilize compositions that contain a bacterial content that provides better environmental fate attributes to both on site waste treatment systems and municipal treatment plants through biological augmentation of the indigenous bio-mass.

The following references may be pertinent to the invention disclosed herein.

PCT Publication WO97/25865 pertains to a sanitizing composition containing a surfactant, a chelating agent, a preservative, a thickening agent and a *Bacillus* microorganism.

U.S. Patent No. 5,449,619 pertains to a drain opener formulation containing a *Bacillus* microorganism and a surfactant as well as a preservative.

U.S. Patent No. 4,839,373 pertains to preservative composition containing quaternary ammonium compounds in conjunction with a specific preservative, which is a derivative of benzothiazole in specific ratios.

U.S. Patent No. 4,404,128 pertains to an enzyme detergent composition where the enzyme is a proteolytic enzyme.

U.S. Patent No. 4,655,794 pertains to a liquid cleaning compound containing abrasive particles plus viable microorganisms, such as, *Bacillus*, a detergent, thickener and an anti-settling agent. The composition is a cleaning composition.

U.S. Patent No. 5,409,546 pertains to a method for cleaning and disinfecting contact lens wherein there is a preservative which is a serine protease derived from bacteria belonging to the genus, *Bacillus*, a metal chelating agent and boric acid. Non-ionic surfactants are also described.

U.S. Patent No. 5,731,278 describes heavy-duty laundry detergents containing surfactants, non-surface active liquid carrier compositions, viscosity enhancing agents and enzymes.

PCT publication WO97/16541 described an alkaline protease, which describes a strain of *Bacillus* and which shows a stability in the presence of surfactants.

PCT publication WO97/38586 discloses a method of preventing the growth of microorganisms other than *Salmonella* on meat products by contacting the meat product with a microbial growth inhibiting amount of a quaternary ammonium compound together with a microorganism, such as *Bacillus*.

SUMMARY OF THE INVENTION

Described is an aqueous disinfectant and hard surface cleaning composition comprising:

an effective disinfecting amount of a quaternary ammonium compound;

an effective amount of a spore forming microbial composition; and

an effective water dispersing amount of a surfactant.

Also described is a method of cleaning a soiled hard surface containing a diverse microbial flora, comprising applying the composition as described above to the surface and drying the surface thereby cleaning the surface.

Also described is a concentrated aqueous disinfectant and hard surface cleaning composition described above useful by diluting the composition with water in an amount of 1-10% by weight of the composition and the rest water.

DESCRIPTION OF PREFERRED EMBODIMENTS

The aqueous disinfectant and hard surface cleaning composition of the present invention utilizes an effective disinfecting amount of a quaternary ammonium compound. The ammonium compound is a cationic detergent which provides excellent activity against bacteria, fungi and enveloped viruses. Additionally, quaternaries offer consistent efficacy in the presence of poor water quality and organic soil load conditions. For a more detailed listing of enveloped viruses, see Fields Virology, 2nd Edition 1990.

Antimicrobial cationics available to the trade.

There are three principal suppliers of quaternary based antimicrobials that are registered as actives for this type of use with the EPA. These companies are Lonza, Stepan and Mason Chemical Company. The trade names under which they are marketed are Bardac, BTC and Maquat respectively. All of the desirable cationic material sold conform to one of the following families:

First Generation:	C_6H_5-$CH_2N(CH_3)_2R$
	Alkyldimethylbenzyl ammonium chloride
Second Generation:	$(C_2H_5)C_6H_5$-$CH_2N(CH_3)_2R$
	Alkyldimethylethylbenzyl ammonium chloride
Third Generation:	$N(R)_2(CH_3)_2$
	R-dimethyl ammonium chloride

The preferred cationic detergent is from the quaternary ammonium chloride family such as the BTC (trademark) materials from Stepan Chemical including dialkyl of from 6-18 carbon atoms dialkyl of from 1-4 carbon atoms ammonium chloride; preferably didecyl dimethyl ammonium chloride, dioctyl dimethyl ammonium chloride, octyl decyl dimethyl ammonium chloride and alkyl (C_{14} - 50%, C_{12}-40%, C_{16}-10%) dimethyl benzyl ammonium chloride. Even more preferably is a blend of the ammonium chloride materials as recited below.

The system utilized in this product is designed to maximize all of the beneficial aspects of quaternary ammonium compounds and consists of the following blend in a 1:1:2:2.67 wt. ratio respectively:

1. Didecyl dimethyl ammonium chloride (BTC 818) (Trademark of Stepan Chemical)
2. Dioctyl dimethyl ammonium chloride (BTC818) (Trademark of Stepan Chemical)
3. Octyl decyl dimethyl ammonium chloride (BTC 818)
4. Alkyl (C_{14}-50% by wt, C_{12}-40% by wt, C_{16}-10% by wt) dimethyl benzyl ammonium chloride. (BTC 835) (Trademark of Stepan Chemical)

During use as a disinfecting composition, the total levels of this blend (1-4) will preferably range from 500 to 1000 ppm's (parts by weight per million).

Other quaternary materials that may be utilized are Tomah quaternaries (trademark of Tomah Products of Milton, Wisconsin for quaternary ammonium materials).

Tomah quaternaries are based on the reaction of high molecular weight aliphatic tertiary amines with an alkylating agent such as

methyl chloride. Quaternaries are more cationic and more stable to pH change than other amine-based surfactants such as ethoxylated amines or amine acetate salts. The different molecular configurations give different solubility, emulsification, and cationic strength properties.

Most Tomah Quaternaries can be represented by the formula where R is an aliphatic hydrophobe.

$$RO(CH_2)_3N^+ (CH_3)(C_2H_4OH)_2Cl^-$$

R is an aliphatic alkyl of hydrophobe (of from 6-18 carbon atoms)

Other useful quaternary ammonium materials from Tomah are:

Q-14-2	75% active isodecyloxypropyl dihydroxyethyl methyl ammonium chloride;
Q-14-2PG	75% active isodecyloxypropyl dihydroxyethyl methyl ammonium chloride (supplied in propylene glycol);
Q-17-2	75% active isotridecyloxypropyl dihydroxyethyl methyl ammonium chloride;
Q-17-2PG	75% active isotridecyloxypropyl dihydroxyethyl methyl ammonium chloride (supplied in propylene glycol);
Q-18-2 (50)	50% active octadecyl dihydroxyethyl methyl ammonium chloride;
Q-18-15	100% active octadecyl poly (15)oxyethylene methyl ammonium chloride;

Q-D-T	50% active tallow diamine diquaternary;
Q-DT-HG	70% active tallow diamine diquaternary (supplied in hexylene glycol);
Q-C-15	100% active coco poly(15)oxyethylene methyl ammonium chloride; and
Q-ST-50	50% active trimethyl stearyl quaternary ammonium material.

The present invention utilizes an effective amount of a spore forming microbial composition. The biological products that are desirable with the present invention are in liquid or lyophilized form and are generally based upon the bacteria from the genus *Bacillus*. These organisms are preferred because they are easy to be formulated due to their ability to go into a dormant spore state. In addition, the organic degradation abilities of certain species within the *Bacillus* genus are appropriate for the types of applications described herein for cleaning purposes. Further, the *Bacillus* bacteria lend themselves readily to large scale fermentation. The bacterial content of the formulations as described herein are desirable based upon their stability in the presence of the other components of the formulation, in particular, the antimicrobial quaternary materials. Preferred organisms are *Bacillus* amyloliquefaciens, *Bacillus* licheniformis, *Bacillus* megaterium and *Bacillus* subtilis. These products are commercially available from a number of sources. The preferred materials of the *Bacillus* genus can be obtained from Semco Laboratories, Inc. available under the name Sporzyme 1B, Sporzyme Ultra Base 2, Sporzyme EB and Sporzyme

BCC (all trademarks of Semco Laboratories for liquid materials containing bacterial spores of the *Bacillus* genus). The *Bacillus* genus materials are also available from Sybron Chemicals, Inc. of Wilmington, DE.

An additional component utilized in the disinfectant cleaning composition of the present invention is a surfactant. The use of surfactants is to assist in decreasing the surface tension of water and remove soils from the substrate. A particularly desirable group of surfactants are those that maintain the stability of the cationic disinfectant and the microbiological materials. The surfactants that are preferably utilized are non-ionic and amphoteric materials. These materials provide efficient wetting of the substrate to be cleaned, emulsification of oily soils and are ionically compatible with the cationic components of the cleaning composition.

Non-ionic materials that may be utilized include fatty amines or oxides, fatty alkanolamides, alkyl polyglucosides and linear alcohol ethoxylates. Preferred surfactants are secondary alcohol ethoxylates, betaines, sultaines and amine oxides. Preferred alcohol ethoxylates and ethoxysulfates are available under the trademark Neodol Chemical Company (trademark for surfactants of Shell). Neodol products include linear primary alcohols in a C_9-C_{15} alkyl range, ethoxylate non-ionic surfactants and ethoxy sulfate.

Further examples of non-ionic surfactants are materials known as Igepal (trademark of Rhodia, Inc. for nonyl phenoxy polyethoxy ethanol); Tergitol NP (trademark of Union Carbide Corp. for nonylphenol ethoxylate); Tergitol 15-S (trademark of Union Carbide Corp. for secondary alcohol ethoxylates); Triton X series (trademark of Union Carbide Corp. for octyl phenol polyethoxylate) and Tween Materials (trademark of ICI

Americas, Inc. for polyoxyethylene (20) sorbitan monostearate and polyoxyethylene sorbitan monooleate). Examples of amphoteric materials include Mirataine CBC and Miranol C2MSF (trademark of Rhodia, Inc. for surfactant) and Lexaine (trademark of Inolex Co. for cocoamidopropyl betaine).

In order to maintain the stability of the dispersion of the microbiological spores that are utilized in the present case and to prevent the spores from settling out, which causes a loss in the effectiveness of a product, thickening agents are utilized. The thickening agents that are desirable are those that are compatible with cationic systems. A preferred thickening agent is a cellulosic material such as hydroxyethylcellulose. Preferred are Natrosol (trademark of Hercules for non-ionionic water soluble polymer hydroxylethyl cellulose) and Cellosize (Trademark of Union Carbide for hydroxymethylcellulose).

An additional thickening agent that may be used is Acusol 880/882 – (Trademark of Rohm and Haas Co. for nonionic associative polymer mixture of polyethylene glycol, propylene glycol and water having a pH of 7-9 and a viscosity of 60,000 CPS maximum).

The formulation for cleaning composition of the present application is as follows:

NAME	CONCENTRATE AMOUNT (% by wt.)	PREFERRED AMOUNT FOR USE
Cationic Material	1-10%, preferably 5.5%	0.1-2%, preferably 0.085%
Microbiological Material	$1 \times 10^9 - 1 \times 10^{12}$, preferably 5.0×10^{11} CFU/gallon	$1 \times 10^8 - 1 \times 10^{10}$, preferably 7.8×10^9 CFU/gallon
Surfactant	1-10%, preferably 6.53%	0.1 to 5%
Thickening Agent	0.01 - 2.0%, preferably 0.25%	(0.0002 - 0.005%) trace
Remaining Amount: Water	Total 100%	

The pH of the composition in the concentrate form ranges from about 6 to 8. The pH in the composition as actually used ranges from about 7 to 8.

A preferred formulation is recited below. The composition is prepared by mixing the ingredients as described.

TABLE I

	Formula (% by wt.)		
	Water	50.00%	pH-8.0 +/-0.2%
	Natrosol 250 HR (hydroxyethyl cellulose thickener)	0.25%	*RIS-13.0% +/-0.2%
	45% Potassium Hydroxide	0.0225%	Specific Gravity ~0.999
	Sodium Chloride	0.2%	
	Q-17-2 (Quaternary)	1.7%	
	Neodol 25-7 (non-ionic surfactant)	5%	
	BTC 818 (Quaternary)	6.53%	
	BTC 835 (Quaternary)	4.35%	
	Fragrance	0.15%	
	Citric Acid	0.01%	
	Water	31.87%	
	Bacteria Cultures	0.01%	
	Dye	0.002%	

*RIS means refractive index of solids.

Mixing instructions:

Add the ingredients in the order above. First, add the water and disperse the Natrosol 250 HR slowly and evenly to the water. Avoid large clumps of Natrasol 250 HR. Once the total amount of the Natrosol 250 HR has been added, add the potassium hydroxide to the solution. Mix well for approximately ten minutes or until the Natrosol 250 HR is hydrated. After the Natrosol 250 HR has been hydrated continue by adding

the salt, and mix for two minutes, or until dissolved. Next, add the Q-17-2 and the Neodol 25-7, mix well for ten minutes or until there are no chunks of undispersed surfactant. Continue by adding the BTC 818 and the BTC 835. After the surfactants are dispersed, add the fragrance and mix until solution becomes clear. Before adding the Bacterial cultures adjust the pH by adding the citric acid. Finally, mix the final water and the bacterial cultures in a separate container. When the Bacterial cultures are completely hydrate, add to the batch. Last, add the dye and mix until dispersed thoroughly.

The formulation as described above in Table I was subjected to bacterial stability tests, namely subjecting the composition to long term stability at room temperature and at a hot box temperature of 100°F.

The Table II below indicates the long term stability of the composition of the invention.

TABLE II

Days	0	7	17	27	34	41	45	46	52	60	87	100
Room* Temp CFU	2.63	2.6	2.7	2.5	2.23	1.6	4.37	2.2	2.33	2.45	1.87	1.9
100°F * CFU	2.63		0.4	1.1	1.17	1.05	0.43	2.17	0.53	0.57	1.0	0.4

CFU = Colony Forming Unit (x 10^7)
*Data given at room temperature and at 100°F

The compositions of the present application can easily be utilized to meet the cleaning performance requirements of different testing techniques. An example of such testing technique is a cleaning verification as described in ASTM D 4488-95 where the natural or accelerated aging of

soil such as baked on greasy soil may be utilized to correlated with actual use. Other actual use tests to determine antimicrobial efficacy are the SARC (semi-automatic ring carrier) modification to and actual AOAC use-dilution method for testing disinfectants. See the AOAC Official Methods Of Analysis, 15th Edition, 1990.

It has been found particularly useful in the testing of Applicant's compositions to utilize nisin in a modification to the AOAC method compositions. Nisin is an antibiotic containing 34 amino acid residues, produced by *streptomyces* lactis.

Explanation of Nisin:

Nisin is not an ingredient in the product formulation. It is a modification to the AOAC test method. Specifically, when setting up the test sub-culture 0.1 μg/ml of nisin is added to the letheen broth. This level of nisin shows no bacteriostatic effect on the test organism, but inhibits out-growth of any *Bacillus* spores which are transferred over on the carrier from the test solution.

The standard "use-dilution" test was run against Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella choleraesuis and Escherichia coli. The inventive composition described in Table I satisfactorily passed such tests.

Other components may be added to the composition without materially modifying the composition such as colorant and fragrance.

The composition as described above is particularly useful for the overall desires of the present application for cleaning and disinfecting hard surfaces.

An additional preferred formulation is recited below. The composition is prepared by mixing the ingredients similar to that described above.

TABLE IV

Formula (% by wt.)		
Water	85.77%	pH-7.0 +/-0.2%
Natrosol 250 HR (hydroxyethyl cellulose thickener)	0.25%	*RIS-13.0% +/-0.2%
45% Potassium Hydroxide	0.0225%	Specific Gravity –0.999
Calcium Chloride	0.2%	
Q-17-2 (Quaternary)	0.6%	
Neodol 1-7 (non-ionic surfactant)	1.69%	
Neodol 1-3	0.56%	
BTC 818 (Quaternary)	6.53%	
BTC 835 (Quaternary)	4.35%	
Citric Acid	.024%	
Bacteria Cultures	$5x10^{11}$/gallon	

*RIS means refractive index of solids.

Stability of the formulation in Table IV is described in Table V, below.

TABLE V

Days	0	7	17	27	34	41
Room* Temp CFU	5.77	5.63	5.1	5.93	5.6	5.2
100°F * CFU	5.77	5.07	4.93	3.4	3.77	3

CFU = Colony Forming Unit (x 10^7)
*Data given at room temperature and at 100°F

The long term stability of the composition may also be illustrated by the % recovery as demonstrated in Table III.

TABLE VI

	Initial Population	35 Days	Net Loss	% Recovery
Room Temperature	5.77×10^7	5.2×10^7	5.7×10^6 CFU/ml	90.1%
100° F	5.77×10^7	3.0×10^7	2.77×10^7 CFU/ml	52.0%

While the forms of the invention herein disclosed constitute presently preferred embodiments, many others are possible. It is not intended herein to mention all of the possible equivalent forms or ramifications of the invention. It is understood that the terms used herein are merely descriptive rather than limiting, and that various changes may be made without departing from the spirit or scope of the invention.

WHAT IS CLAIMED IS:

1. An aqueous disinfectant and hard surface cleaning composition comprising:

an effective disinfecting amount of a quaternary ammonium compound;

an effective amount of a spore forming microbial composition; and

an effective water dispersing amount of a surfactant.

2. A concentrated aqueous disinfectant and hard surface cleaning composition, useful by diluting with water, comprising:

an effective disinfecting amount of a quaternary ammonium compound;

an effective amount of a spore forming microbial composition;

an effective water dispersing amount of a surfactant; and

an effective amount of a thickening agent.

3. The composition of claim 1 wherein the cleaning composition is present in the amount of 1 to 10% by wt. with the remainder of the composition being 90 to 99% by wt water.

4. The composition of claim 3 wherein the quaternary ammonium compound is present in the amount of 5.5%;

the spore forming microbial composition is present in the amount of 0.01%;

the surfactant is present in the amount of 6.3%;

and the pH ranges from 6 to 8.

5. The composition of claim 1 comprising the following materials by weight:

quaternary material	1-10%
microbial material	$1 \times 10^9 - 1 \times 10^{12}$ CFU/gallon (colony forming unit)
surfactant	1-10%
a thickening agent	0.1-5%
water	remaining amount
	total 100%.

6. The composition of claim 1 comprising the following materials:

quaternary material	0.1-2% by wt.
microbial material	$1 \times 10^8 - 1 \times 10^{10}$ CFU/gallon
surfactant	0.1-5%
a thickening agent	trace
water	remaining amount
	total 100%.

7. A method of cleaning a soiled hard surface containing a diverse microbial flora comprising applying the composition of claim 1 to the surface and drying the surface thereby cleaning and disinfecting the surface.

8. The method of claim 7 wherein the hard surface contains microbes, selected from the group consisting of Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella choleraesius and Escherichia coli.

9. The method of claim 7 wherein the soiled surface is comprised of blood serum as an organic soil load in the composition which is diluted in hard water containing 100-400 ppm $CaCO_3$, thereby demonstrating efficacy as a one-step cleaner disinfectant.

10. The method claim 7 comprising the following materials:

quaternary material	1-10%
microbial material	$1 \times 10^9 - 1 \times 10^{12}$ CFU/gallon (colony forming unit)
surfactant	1-10%
a thickening agent	0.1-5%
water	remaining amount
	total 100%.

11. The method of claim 7 comprising the following materials:

quaternary material	0.1-2% by wt.
microbial material	$1 \times 10^8 - 1 \times 10^{10}$ CFU/gallon
surfactant	0.1-5%
a thickening agent	trace
water	remaining amount
	total 100%.

12. An aqueous disinfectant and hard surface cleaning composition consisting essentially of by weight:

cationic material	1-10%
microbiological material	$1 \times 10^9 - 1 \times 10^{12}$ CFU/gallon
surfactant	1-10%
thickening agent	0.1-5%
water	remaining amount total 100%.

13. The composition of claims 1 or 12 where the salt used is calcium chloride.

14. The method of claims 10-11 where the salt used is calcium chloride.

15. The composition of claim 1, wherein the ammonium compound is a dialkyl of from 6-18 carbon atoms, dialkyl of 1 to 4 carbon atoms ammonium compound.

16. The composition of claim 2, wherein the ammonium compound is a dialkyl of from 6-18 carbon atoms, dialkyl of 1 to 4 carbon atoms ammonium compound.

17. The composition of claims 1, wherein the *Bacillus* material is comprised of *Bacillus* subtilis.

18. The composition of claims 1, wherein the *Bacillus* material is comprised of *Bacillus* subtilis.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/48 C11D3/38 C11D1/835 A01N63/00 A01N33/12
//C11D1/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 25865 A (SYBRON CHEMICALS) 24 July 1997 (1997-07-24) cited in the application	1-3, 5-12, 15-18
A	page 5, line 10 - line 12; example 1	4
Y	WO 99 16854 A (RECKITT & COLMANN PROD LTD) 8 April 1999 (1999-04-08)	1-3, 5-12, 15-18
A	abstract; table 1	4

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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(54) Title: CLEANING SOLUTION TO REMOVE HYDROCARBONS FROM A SUBSTRATE

(57) Abstract: A method for the cleaning of a substrate having an organic compoud such as a hydrogenic compound thereon, the method comprising the step of applaying to the substrate a composition comprising a lignosulfonate and a microbially effective amount of microorganism in an aqueous solution. The method is ideally practiced to achieve the microbial degradation of hydrocarbons and can be used as a parts washing solution and for cleaning substrates such as floors, decks of vessels, etc.

CLEANING SOLUTION TO REMOVE HYDROCARBONS FROM A SUBSTRATE

FIELD OF THE INVENTION

The present invention relates to a cleaning or washing solution and to a method of cleaning or washing hydrocarbon based material from a substrate.

BACKGROUND OF THE INVENTION

Solvents are widely used in various automotive and industrial parts washing equipment. As such, petroleum based solvents and even ordinary aqueous cleaners require periodic disposal of the contaminated solution by expensive hazardous waste hauling services. In turn, these services are required to treat the contaminated solution. It has been proposed in the art to use organic microbial cleaning solutions to replace such solvents and aqueous cleaning solutions. However, the cost of doing so has been substantial and accordingly, the process has not gained a wide degree of acceptance to date.

The use of microbes for the microbial degradation of hydrocarbons by treating the same with particular microorganisms which are capable of using the hydrocarbon as an energy and carbon source is well known in the art. The process has been used to clean up oil spillage as it has occurred on various waterways. It is also being used for the cleaning of oil transport vessels and/or storage tanks. However, the process is relatively expensive to practice.

Many different types of hydrocarbons are utilized in different industrial applications. Hydrocarbons are generally derived from petroleum based materials and

are a complex mixture of straight chain and branched alkanes or alkenes, saturated ring compounds and aromatic compounds. Industrial hydrocarbon products include gasoline, kerosene, burner fuel oil, diesel oil, gas turbine oil, aviation fuels, lubricating oils and hydrocarbon greases. As will be appreciated, such products have a widespread use and it is frequently necessary to clean up spills or other contamination of a substrate by such hydrocarbon products.

In the art, various methods for cleaning hydrocarbon contaminated substrates have been proposed. These include the physical removal of the product by use of absorption media, dispersal detergents, microbial degradation, agglomeration, and the use of organic chemicals.

For many years, hydrocarbon contamination was not considered a problem and the procedure for controlling environmental damage was to ship the undesirable contaminants to a secure landfill. However, this is no longer an option in environmentally sensitive areas and many countries and other jurisdictions are adapting strict regulations concerning the disposal of hydrocarbons. Furthermore, this method entails a substantial expense and represents a large potential liability.

It is also known in the art to use biological materials such as bacteria and enzymes to degrade hydrocarbon. Given sufficient time, the bacteria or enzymes can naturally degrade the hydrocarbon contaminants. Thus, as shown in U.S. Patent 3,152,983, one may use a microbial method for the disposal of oil waste. U.S. Patent 3,871,956 teaches a method for cleaning accidental oil spills on water or in a soil using a microbial method.

While such methods are known and have been proposed for a number of years, the commercial use of these methods has been rather limited due to time limitations and ineffectiveness.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a microbial cleaning composition which is both effective and cost efficient.

It is a further object of the present invention to provide a method for cleaning a substrate having hydrocarbons thereon, and which process is environmentally friendly and relatively inexpensive.

According to one aspect of the present invention, there is provided a method of cleaning a substrate having an organic compound thereon, the method comprising the step of applying to the substrate a composition comprising a lignosulfonate and a microbially effective amount of microorganisms in an aqueous solution.

According to a further aspect of the present invention, there is provided a method for the preparation of a cleaning mixture for use in cleaning a substrate, the method comprising the steps of providing ammonium lignosulfonate, adjusting the pH of the ammonium lignosulfonate to a pH value of between 6.5 and 7.5, and adding a microbially effective amount of hydrocarbon degrading bacteria to the ammonium lignosulfonate.

According to a further aspect of the present invention, there is provided a cleaning solution comprising ammonium lignosulfonate, a microbially effective amount of hydrocarbon degrading bacteria mixed with the ammonium lignosulfonate,

the ammonium lignosulfonate being pH adjusted to a pH value of between 6.5 and 7.5.

In a greater detail, the lignins are a natural complex polymer which are generally produced as a co-product of the paper industry, the lignins being separated from the trees by a chemical pulping process. Lignosulfonates are also known as lignin sulfonates and sulphite lignins are products of sulphite pulping. Other delignifying technologies may include the use of an organic solvent or high pressure steam treatment to remove lignins from plants.

As aforementioned, lignin is a very complex natural polymer, the exact chemical structure not being known. Physical and chemical properties can differ depending on the extraction technology. Lignosulfonates have typically been used for their dispersing, binding, complexing and emulsifying properties. Lignins have been used for many years and extensive studies have been done to test lignin impact on the environment. To date, lignins have been shown to be safe and not harmful to plants, animals and aquatic life when properly manufactured and applied. Furthermore, lignosulfonates have been found to be essentially non-toxic and non-irritating, non-mutagenic nor toxic and may be widely used in animal and human feed contact products.

The particular microbe or microbes used in conjunction with the lignosulfonates may be selected from among those known to have the property to degrade hydrocarbons. Several such microbes are described in the literature and are commercially available for the specific purpose of degrading hydrocarbons such as

petroleum products.

Surprisingly, it has been found that the use of the lignosulfonate with the microbes is a very efficient and cost effective way of cleaning hydrocarbon containing substrates. Without being limited to any particular theory, it is thought that the lignosulfonates provide a readily available food source for the microbes and the lignosulfonate also helps in the cleaning. As such, the microbes are in a healthy and active state when they are placed in contact with the hydrocarbons and hence are able to reactivate themselves very quickly and thus are highly effective.

As aforementioned, the microbes may be selected from those known in the art. Such may include microorganisms of the genus *Achromobacter, Actinobacter, Alcaligenes, Arthrobacter, Bacillus, Flavobacterium, Pseudomonas*, and mixtures thereof. Particularly preferred are those naturally occurring non toxigenic microorganisms of the genus *Bacillus, species subtilis, licheniformis, and polymyxa.*

The microbial content may vary and again, is within the skill of those knowledgeable in the art to use a suitable concentration for a given condition. In a preferred embodiment, a concentrate with a viable bacterial content (CFU) in the billions of organisms per gram may be utilized. After mixing with the lignosulfonate, the concentrate may form between 0.5% to 5% by weight of the composition and with a microbial content in excess of 50,000 CCU per gram. The various strains of microorganisms can degrade and detoxify a large range of substituted and unsubstituted aliphatic and aromatic hydrocarbons.

Preferably, the composition is adjusted to have a pH of between 6.5 and 7.5

and preferably in the range of 7 (neutral). In order to do so, the naturally acidic lignosulfonate which has a pH of between 4 and 5, may have lime added thereto in an amount sufficient to bring the pH to approximately 7.

Generally, the microbial content will attack and degrade phenol, benzene, toluene, other aromatic hydrocarbons with hydroxylated, nitrogenated groups, octane, ethane, and other short-chained alkyl hydrocarbons; salicylic acid, biphenyl, xylol, phenoxy alcohols, mineral oils, lubricating oils, kerosene, surfactants, gasoline, pentachlorophenol, intermediate length alkyl hydrocarbons and alcohols, fatty acids, benzolic acid and citrus oils; complex dyes, lignins, starchy complexes, carbohydrate by-product waste, wood pulp waste, structural board and pressboard waste, distillery waste, wood preservative waste, cresols, creosote, naphthalene, ethylene glycol, and heterogeneous aromatic hydrocarbon waste, protein complex wastes, oleaginous waxes or fats containing wastes, wastes with fats & oils and dissolved aromatics, hydrocarbons linked with aminos, glycerol esters; treating fuel oils, intermediate levels of moderate molecular weight hydrocarbon contamination in soil or aqueous environment, heavier machine oil, heavier grade lubricating oil; and waste from petrochemical plants, refineries, chemical formulators, pharmaceutical processors, pulp and paper mills, wood processing and treatment plants, metal machining and fabrication plants, distilleries, textiles and food processing.

The composition is not flammable and contains no known carcinogenes and is both environmentally and people friendly. The microbial stains are able to degrade the various carbon sources at temperatures ranging between 4°C and 45°C.

The composition of the present invention may be utilized for a number of different uses. A prime use would be in a reservoir of a re-circulating parts washing sink. Used in such an environment, the composition maintains a cleaning capability and therefore a higher cost effectiveness. The product may be used on any suitable substrate from which hydrocarbons must be removed. The product is an efficient means to treat clarifiers and wastewater storage tanks for reduction of sludge build up and to decrease odor problems and the frequency of pump outs of the waste.

Conveniently, the composition may be either used as a dry composition to be applied to the locust to be treated or alternatively, and more preferably, is used in the liquid phase. As such, the dry composition may be mixed with water in a weight volume ratio of between 2:1 and 20:1 (grams/liters).

DETAILED DESCRIPTION OF THE EXAMPLES

Having thus generally described the invention, reference will be made to the accompanying examples illustrating embodiments thereof.

Example 1

On a commercially operating dredge, a product comprising ammonium lignosulfonate (86.2% by weight) and a microbial content from a product marketed under the trademark BioZyme-6000 PC available from Ultra Biologics (1.7% by weight) in a concentration of 1.7%. The composition was adjusted to a pH of approximately 7 using lime (12.1% by weight).

The product was used in a conventional parts washing sink aboard the dredge H.R. Morris and for cleaning the bildge of work boats and tenders. The product was

also used on a floating crane and the product was shown to be effective cleaning oil and hydraulic fluid drippings on exterior decks to make the deck a safer work environment for the crew.

A secondary advantage of the product is that all caustic and toxic cleaners aboard the vessels were removed leading to higher cost effectiveness and also to gain control over the possibility of toxic chemicals spilling or leaking.

Example 2

The product of Example 1 has been used in a factory operation to clean oily production floors as well as a cleaner for machine scrubbing and hand mopping operations. The product is highly advantageous and does not leave a typical soap film residue and is also able to treat the mop water with hydrocarbon degrading microbes in the filtering and storage modes. It is believed that use of the product will enable direct discharge of the cleaning fluid.

The product was used for the cleaning of buses and performed very satisfactorily. The concrete floor of a bus washing area was black with oil that had, over the years, penetrated the pores of the concrete. After a few weeks of using the product for bus cleaning, white spots of concrete began to appear as the microbes were degrading the oil in the concrete pores.

In one embodiment, the cleaning solution may also include a citrus component to enhance the cleaning effectiveness of the solution. Many such citrus components are known in the art and are commercially available. The citrus component may be present in any desirable amount subject to it providing an enhanced cleaning

effectiveness and a non-deleterious effect on the bacteria. In this regard, it is important that the solution be designed keeping in mind that certain citrus components can be harmful to certain bacteria. Accordingly, it is necessary to ensure that the combination of a particular bacteria and a particular citrus formulation are compatible.

In a preferred embodiment, the cleaning solution will use ammonium lignosulfonate in a dry powder form, a suitable microbe capable of degrading hydrocarbons, and a pH adjusting agent. The pH adjusting agent will be a material capable of raising the pH such as lime. An advantage of this dry mixture will be the shelf life and ease of shipping.

I CLAIM:

1. A method of cleaning a substrate having an organic compound thereon, the method comprising the step of applying to the substrate a composition comprising a lignosulfonate and a microbially effective amount of microorganisms in an aqueous solution.

2. The method of Claim 1 wherein said bacteria are present in a concentration of between 0.5% and 5%.

3. The method of Claim 1 wherein said bacteria are hydrocarbon degrading bacteria and said lignosulfonate is ammonium lignosulfonate.

4. The method of Claim 3 wherein said ammonium lignosulfonate is diluted in an aqueous solution at a concentration of between 2:1 and 20:1 (grams/liters).

5. The method of Claim 1 wherein said substrate is a floor.

6. The method of Claim 1 wherein said substrate is a deck of a marine vessel.

7. The method of Claim 1 wherein said substrate is a part of a motor vehicle.

8. The method of Claim 3 wherein said composition contains between about 80% to 91.5% by weight of ammonium lignosulfonate, between about 8% and about 15% by weight of a pH adjusting agent, and between about 0.5% and about 5% by weight of a concentrated microbial product of the genus *Bacillus*.

9. A method for the preparation of a cleaning mixture for use in cleaning a substrate, the method comprising the steps of providing ammonium lignosulfonate, adjusting the pH of said ammonium lignosulfonate to a pH value of between 6.5 and 7.5, and adding a microbially effective amount of hydrocarbon degrading bacteria to

said ammonium lignosulfonate.

10. The method of Claim 9 wherein the step of adding a microbially effective amount of hydrocarbon degrading bacteria comprises the step of adding bacteria from the genus *Bacillus* to said ammonium lignosulfonate.

11. The method of Claim 10 wherein the step of adjusting the pH of said ammonium lignosulfonate comprises the step of adding lime.

12. A cleaning solution comprising ammonium lignosulfonate, a microbially effective amount of hydrocarbon degrading bacteria mixed with said ammonium lignosulfonate, said ammonium lignosulfonate being pH adjusted to a pH value of between 6.5 and 7.5.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D1/30 C11D3/38 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° *Special categories of cited documents:*

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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Serbetsoglou, A

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